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Short communication

Why wastewater sludge stimulates and accelerates removal of PAHs in polluted soils?

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ABSTRACT

Wastewater sludge is used worldwide to dissipate hydrocarbon in PAHs-polluted soils. However, little is known about why wastewater sludge stimulates and accelerates the removal of polycyclic aromatic hydrocarbons (PAHs) from soils. Soil of the former lake Texcoco with pH 9 and electrical conductivity $7\,\mathrm{dS\,m^{-1}}$ was contaminated with phenanthrene and anthracene, and amended or not with wastewater sludge sterilized or not, and with or without polyacrylamide while phenanthrene and anthracene were monitored in an aerobic incubation experiment of 112 days. An agricultural soil from Acolman and wastewater sludge treated in the same way served as controls. After 112 days, the largest dissipation of anthracene and phenanthrene was found in the Acolman soil amended or not with wastewater sludge with or without polyacrylamide. The largest dissipation of anthracene and phenantrene from both soils was found in soils amended with wastewater sludge and polyacrylamide, while the lowest degradation of PAHs was detected in unamended PAHs-polluted sludge and in soils amended with sterilized wastewater sludge. It was found that polyacrylamide accelerated removal of PAHs from soils, while wastewater sludge increased the removal of PAHs from soils but the effect is controlled by the physical, chemical and microbial soil properties, the contaminant and microorganisms in wastewater sludge.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have two or more fused benzene rings with natural as well as anthropogenic sources. They are widely distributed environmental contaminants that have detrimental biological effects, toxicity, mutagenecity and carcinogenicity. Due to their ubiquitous occurrence, recalcitrance, and bioaccumulation potential the PAHs have gathered significant environmental concern. They do not degrade easily under natural conditions and their persistence increase with increase in the molecular weight. Although PAHs may undergo adsorption, volatilization, photolysis, and chemical degradation, microbial degradation is the major degradation process. PAHs degradation depends on the environmental conditions, number and type of the microorganisms, nature and chemical structure of the chemical compound being degraded. They are biodegraded/biotransformed into less complex metabolites, and through mineralization into inorganic minerals, H_2O, CO_2 (aerobic) or CH_4 (anaerobic). The rate of biodegradation depends on pH, temperature, oxygen, microbial population, degree of acclimation, accessibility of nutrients, chemical structure of the compound, cellular transport properties, and chemical partitioning in growth medium (Haritash and Kaushik, 2009). PAHs have gathered significant concern because of their presence in all components of environment, resistance towards biodegradation, potential to bio-accumulate and carcinogenic activity.

Additionally, PAHs are produced in many processes, including the burning of fossil fuels, manufacture of gas and coal tar, wood processing, escaped automobile gasoline, fuel-burning kitchen stove and the incineration of wastes (Das et al., 2008). Although several hundred PAHs exist, most studies focus on a limited number of them, namely 16 PAHs listed by the US Environmental Protection Agency (USEPA) and the European Community as pollutants (Puglisi et al., 2007). Concerns over their adverse health effects have resulted in extensive studies on the remediation of PAHs-polluted soil.

According to United Nations Human Settlements Programme (UN-HABITAT, 2008) the 17 registered countries produce ca.

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20 millions of dry metric tons year^{-1} of wastewater sludge, but the real quantity of wastewater sludge produced around the world is far larger. At today, wastewater sludge is used to produce energy and to improve the physical and chemical soil properties. Additionally, wastewater sludge is used to remediate PAHs-polluted soils because it contains nutrients, organic matter and microorganisms able to dissipate PAHs (Bello, 2007; Fernández-Luqueño et al., 2011, 2012).

Wastewater sludge has been used to dissipate PAHs throughout the world. Contreras-Ramos et al. (2008) remove phenanthrene, anthracene and benzo[*a*]pyrene from soils amended with wastewater sludge or vermicompost of wastewater sludge in a 112 day-experiment carried out under laboratory conditions. Additionally, Wlodarczyk-Makula (2010) stated that the addition of wastewater sludge was capable to remove 26% of 16 PAHs according to USEPA from an agricultural soil, while Juteau et al. (2003) found that the wastewater sludge increased the biodegradation of hydrocarbons in a soil spiked with PAHs.

In earlier studies, Fernández-Luqueño et al. (2008, 2009) found that after 112 days, polyacrylamide accelerated the removal of anthracene from an alkaline–saline soil and an agricultural soil, and phenanthrene in an agricultural soil of Acolman. Additionally, they found that concentrations of CO_2, NO_3, NO_2 and NH_4 were also affected during the PAHs dissipation process. However, there is still a gap of knowledge about (i) which wastewater characteristics increased the dissipation of PAHs, and (ii) how large the dissipation is. Hence, the objectives of the present research were: (i) to determinate why wastewater sludge stimulates and accelerates the removal of PAHs from polluted soils, and (ii) to quantitatively assess the wastewater sludge intrinsic capacity for PAHs dissipation.

2. Materials and methods

Area description, soil sampling, soil preparation, and PAHs and sludge characteristics may be found in Fernández-Luqueño et al. (2008, 2009). Soils and sludge properties may be found in Table 1. Methodologies for chemical analysis, PAHs analysis, and statistical analysis may also be found in Fernández-Luqueño et al. (2008, 2009).

Table 1
Characteristics of the Texcoco and Acolman soil and the wastewater sludge.

	Acolman soil	Texcoco soil	Sludge
pH_{H2O}	6.0	9.3	6.4
Water holding capacity (g kg^{-1})[a]	674	659	ND[b]
Water content (g kg^{-1})	76	150	793
Organic carbon (g kg^{-1})	8.1	58.2	509
Inorganic carbon (g kg^{-1})	0.2	0.8	ND
Total Kjeldahl nitrogen (g kg^{-1})	0.7	1.2	27.7
N-NH_4^+ (mg kg^{-1})	3.4	3.7	500
N-NO_3^- (mg kg^{-1})	53	30	86
N-NO_2^- (mg kg^{-1})	0.6	0.3	7.9
Total phosphorus (g kg^{-1})	0.2	0.3	1.7
Extractable phosphorus (mg kg^{-1})	2.0	0.3	600
Electrical conductivity (dS m^{-1})	2.4	7.3	5.7
PAHs (mg kg^{-1})	NDT[c]	NDT	NDT
Clay (g kg^{-1}l)	38	58	ND
Silt (g kg^{-1})	267	80	ND
Sand (g kg^{-1})	695	862	ND
Textural classification	Sandy loam	Loamy sand	ND

[a] On a dry base.
[b] Not determined.
[c] Not detected.

Table 2
Treatments applied to the Texcoco (TEX) and Acolman (ACOL) soil.

Treatment	Characteristics
TEX-SLUDGE-POLY	Soil[a] + phenanthrene[b] + anthracene[c] + sludge-with poly[d]
TEX-SLUDGE	Soil + phenanthrene + anthracene + sludg[e]
TEX-STERILE-SLUDGE	Soil + phenanthrene + anthracene + sterilized dry sludge[f]
TEX-PAH	Soil + phenanthrene + anthracene
ACOL-SLUDGE-POLY	Soil[a] + phenanthrene[b] + anthracene[c] + sludge-with poly[d]
ACOL-SLUDGE	Soil + phenanthrene + anthracene + sludg[e]
ACOL-STERILE-SLUDGE	Soil + phenanthrene + anthracene + sterilized dry sludge[f]
ACOL-PAH	Soil + phenanthrene + anthracene
SLUDGE-PAH	Sludge + phenanthrene + anthracene

[a] 20 g dry soil.
[b] 1200 mg phenanthrene kg^{-1} dry soil.
[c] 520 mg anthracene kg^{-1} dry soil.
[d] 108 g dry sludge flocculated with polyacrylamide kg^{-1} dry soil.
[e] 108 g dry sludge without polyacrylamide kg^{-1} dry soil.
[f] 108 g sterilized dry sludge flocculated with polyacrylamide kg^{-1} dry soil.

2.1. Treatments and experimental set-up

Sub-samples (189) of 20 g soil of each of the six soil samples (three plots × two soils) were added to 120 mL glass flasks. Twenty-one flasks were used for each of the nine treatments (Table 2). The wastewater sludge used in the STERILE treatment was sterilized three times with pressurized steam at 121 °C supplied by an autoclave for 30 min with an interval of a day.

Three flasks were chosen at random from each treatment of the six soil samples, i.e., 189 sub-samples. One and half g soil was extracted for PAHs with acetone and analyzed on a GC. The remaining 18.5 g soil was frozen at −20 °C. These provided zero-time samples. The remaining flasks were placed in 945 mL glass jars containing a vessel with 10 mL distilled H_2O and a vessel with 20 mL 1 M NaOH to trap CO_2 evolved. The jars were sealed and stored in the dark for 112 days at 22 ± 2 °C. After 3, 7, 14, 28, 56 and 112 days, three jars were selected at random from each treatment and the soil was analyzed for PAHs as mentioned before. Every third day the remaining flasks were opened and aired for 10 min to avoid anaerobic conditions, sealed and further incubated.

All data presented were the mean of three replicates in soil from three different flasks ($n = 27$), sampled after 3, 7, 14, 28, 56, and 112 days.

3. Results

After 112 days, the largest dissipation of anthracene and phenanthrene was found in the Acolman soil amended or not with wastewater sludge with or without polyacrylamide (Table 3). Acolman and Texcoco unamended soils dissipated PAHs at lower rate than soils added with wastewater sludge. Texcoco soil amended with sterilized wastewater sludge dissipated only 12% of anthracene and 74% of phenanthrene, while Acolman soil amended with sterilized sludge dissipated 70% of anthracene and 98% of phenanthrene at 112 days. Unamended wastewater sludge polluted with PAHs dissipated only 8% of anthracene and 51% of phenanthrene (Table 3).

The largest dissipation of anthracene and phenanthrene from both soils was found in soils amended with wastewater sludge and polyacrylamide, while the lowest degradation of PAHs was detected in unamended PAHs-polluted sludge and in soils amended with sterilized wastewater sludge (Table 3).

On the scatter plot, the treatments are clearly separated from each other (Fig. 1). Acolman PAHs-polluted soil treated with wastewater sludge can be found in the upper right quadrant while

Table 3

Dissipation of phenanthrene and anthracene in Acolman and Texcoco soil amended with wastewater sludge with or without polyacrylamide, sterilized or left unamended, incubated aerobically at 22 ± 2 °C for 112 days.

Anthracene dissipation/mg kg^{-1} dry soil

Days Treatments	3	7	14	28	56	112	MSD
TEX-SLUDGE-POLY	168 AB a	166 BC a	142 CD a	206 CD a	194 DE a	300 ABC a	172.7
TEX-SLUDGE	107 BC a	112 BCD a	131 CD a	132 DE a	137 E a	211 DE a	123.9
TEX-STERILE-SLUDGE	44C a	28CD a	61 DE a	41 EF a	32 F a	69 DE a	164.9
TEX-PAH	164 AB a	243 AB a	265 AB a	253 BC a	259 CD a	265 BC a	122.2
ACOL-SLUDGE-POLY	196 AB b	243AB b	261 AB b	355 AB a	418 A a	443 A a	91.0
ACOL-SLUDGE	178 AB b	184 B b	188 BC b	354 AB a	354 AB a	389 AB a	96.2
ACOL-STERILE-SLUDGE	212 AB c	231 AB bc	235 BC bc	319 ABC ab	322 BC ab	360 ABC a	96.72
ACOL-PAH	267 A c	344 A bc	368 A ab	420 A ab	432 A ab	437 A a	89.1
SLUDGE-PAH	4C d	7 D d	8 E d	15 F c	31 F b	42 E a	5.5
MSD	119.9	140.5	116.6	115.4	90.4	155.2	

Phenanthrene dissipation/mg kg^{-1} dry soil

Days Treatments	3	7	14	28	56	112	MSD
TEX-SLUDGE-POLY	547 BC c	663 BC bc	693 BC bc	793 C b	848 B ab	1021 ABC a	208.6
TEX-SLUDGE	720 AB b	756 BC ab	809 BC ab	815 BC ab	814 B ab	922C a	183.0
TEX-STERILE-SLUDGE	583 ABC b	622CD b	711 BC ab	718C ab	730 BC ab	885C a	234.4
TEX-PAH	666 AB b	740 BC ab	705 BC ab	686C b	710 BC ab	982 BC a	285.1
ACOL-SLUDGE-POLY	819 A b	831 AB b	900 AB b	1131 A a	1187A a	1194 A a	158.9
ACOL-SLUDGE	676 AB b	689 BC b	689 BC b	1008 AB a	1047 A a	1181 AB a	215.8
ACOL-STERILE-SLUDGE	783 AB b	798 ABC b	835 AB b	1058 A a	1170 A a	1185 AB a	208.7
ACOL-PAH	682 AB c	991 A b	1089 A ab	1137 A a	1139 A a	1143 AB a	115.5
SLUDGE-PAH	412C b	428 D b	569 C ab	612C a	590C a	609 D a	157.1
MSD	252.6	202.4	264.2	204.4	147.0	210.6	

Value with the same capital letters are not significant different by treatment. Value with the same letters are not significant different by time.

unamended PAH-polluted wastewater sludge lie in the lower left quadrant (Fig. 1a). Texcoco PAHs-polluted soil amended with wastewater sludge can be found in the upper right quadrant while unamended PAHs-polluted wastewater sludge lie in the lower left quadrant (Fig. 1b). The PAHs dissipation improved in the following order SLUDGE-PAH < TEX-SLUDGE = TEX-STERILE-SLUDGE < TEX-PAH < TEX-SLUDGE-POLY < ACOL-SLUDGE = ACOL-STERILE-SLUDGE = ACOL-PAH < ACOL-SLUDGE-POLY treatment.

4. Discussion

It is well known that several environmental factors, e.g., organic matter, clay minerals, temperature, water content, pH, salinity, Na^+, Cl^-, CO_3^{2-}, and SO_4^{2-} content, particle and pore-size distribution, supply of oxygen, C/N ratio, and bioavailability of inorganic nutrients affect biodegradation of organic contaminants in soil, while salinity impede rapid removal of hydrocarbons from soil as microbial activity is inhibited, but addition of wastewater sludge might alter soil characteristics and provide nutrients and microorganisms to accelerate their dissipation.

Our data suggest that the polyacrylamide accelerated removal of PAHs from the Acolman and Texcoco soil may be an effect of the N release upon polyacrylamide decomposition, further suggesting that polyacrylamide enhanced the dissipation of PAHs. Sojka et al. (2007) stated that polyacrylamide affects physical processes such as adsorption of PAHs on the soil matrix thereby augmenting their bioavailability and degradation. Moreover, Wen et al. (2010) found microorganisms able to degrade polyacrylamide from activated sludge and oil-contaminated soil. In addition, it is well known that polyacrylamide restores the soil structure and improves the soil aggregate stabilization (Hu et al., 2012), so that the polyacrylamide and/or its decomposition might increase the oxygen supply, regulate the water content and improve the nutrients bioavailability in order to increase the PAHs dissipation.

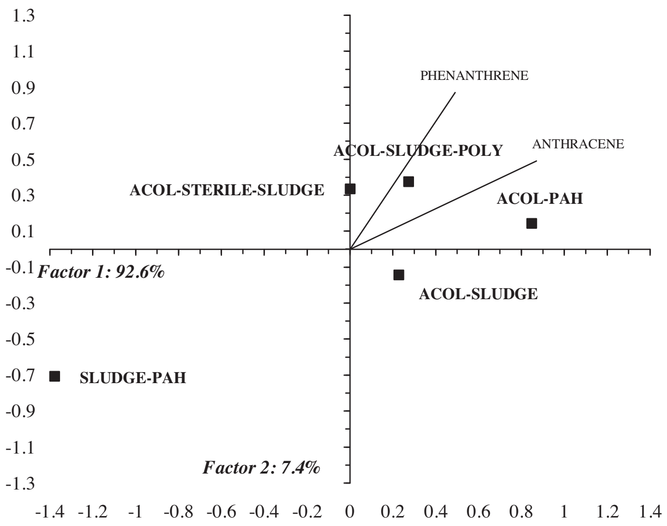
Texcoco soil amended with sterilized wastewater sludge dissipated only 12% of anthracene and 74% of phenanthrene, while Acolman soil amended with sterilized sludge dissipated 70% of anthracene and 98% of phenanthrene at 112 days. Phenanthrene was rapidly removed from the Acolman and Texcoco soil in spite of its high initial concentration (1200 mg kg^{-1}). Mueller and Shann (2006) attributed the fast dissipation of phenanthrene to its high bioavailability and to the capacity of microorganisms to degrade it. The slower degradation on anthracene can be attributed to its low solubility in aqueous systems (0.07 mg L^{-1}) compared to that of phenanthrene (1.29 mg L^{-1}), which renders it only slowly available for microbial degradation.

It was found that unamended wastewater sludge spiked with PAHs dissipated only 8% of anthracene and 51% of phenanthrene. However, wastewater sludge has been used to remediate PAHs-polluted soils during many decades. It is understood that wastewater sludge contains nutrients, organic matter, polyacrylamide and microorganisms to improve the PAHs dissipation when it is mixed with soil, but these data suggest that the interrelationship between wastewater sludge and soil is very important to increase the dissipation of hydrocarbons in a PAHs-polluted soil.

The dissipation of PAHs decreased significantly in soils amended with sterilized wastewater sludge. It implies that wastewater sludge contains microorganisms able to dissipate PAHs and/or that some physical or chemical properties from wastewater sludge are affected during the sterilization process. However, Fernández-Luqueño et al. (2008) did not find changes neither in CO_2 emission, nor in NO_3^-, NO_2^-, and NH_4^+ concentrations from sterilized wastewater sludge compared to unsterilized wastewater sludge. Additionally, it has been demonstrated that changes in pH as effect of wastewater sludge addition or nutrients from the wastewater sludge had no significant effect on the PAHs dissipation in soil spiked with phenanthrene and anthracene (Fernández-Luqueño et al., 2008).

It implies that wastewater sludge stimulates and accelerates the dissipation of anthracene and phenanthrene from PAHs-polluted soil as effect of the polyacrylamide content and its microbial community but not by pH change or by its nutrient

a) Acolman soil



b) Texcoco soil

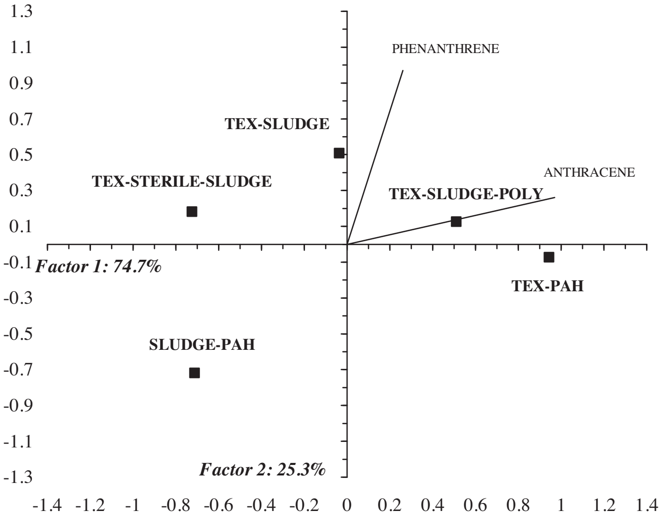


Fig. 1. Principal component analysis of PAHs dissipation in an agricultural soil (a) or in a saline–alkaline soil (b), amended or not with waste water sludge. Treatments description can be found in Table 2.

concentrations. In Addition, it has to be remembered that polyacrylamide increases the nanoparticles concentration in wastewater sludge, which might have improved the PAHs dissipation (Fernández-Luqueño et al., 2014).

5. Conclusion

It was found that polyacrylamide accelerated the removal of PAHs from soils, while wastewater sludge increased the removal of PAHs from soils but the effect is controlled by the physical, chemical and microbial soil properties, the contaminant and microorganisms in both soil and wastewater sludge. Wastewater sludge polluted with PAHs must be treated with remediation technologies before its final disposal; otherwise the PAHs contamination will be persistent.

Conflict of interest

The authors declare that they have no conflict of interest.

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